

The Breakdown of Clapeyron-Clausius Equation as the Result of Irreversibility of the Phase Transitions of the First Kind

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It is shown if the phase transitions of the first kind (PT1) are irreversible, then in the Clapeyron-Clausius equation (CCE) one must substitute the inequality

$$dT_m / dP \leq \Delta V_m / \Delta S_m, \quad (1)$$

where P is the pressure, T_m is the temperature of PT1, ΔV_m and ΔS_m are the changes at PT1 of volume and entropy, respectively. It is pointed out that the sign of equality in (1) is admitted only at the "limit of reversibility of PT1", i.e. at the conditions: $\Delta V_m \rightarrow 0$, $\Delta S_m \rightarrow 0$, $\Delta V_m / \Delta S_m = \text{const}$. Only in this case the inequality (1) is transformed in to CCE.

In the analysis of experimental data for melting and polymorphous PT1 it is shown that if the change of volume is a few per cents (as occurs for melting of metals), then inequality (1) is not shown to be significant and because it can be used in the form of CCE. But if the change of volume at PT1 is sufficiently large (for example, in the melting of alkali halides crystals (AHC), or at boiling PT1 and sublimation PT1), then the excess of right side than left side in (1) can lead to the significant errors when the CCE is applied to calculations. Experimental works, where the significant breakdowns of CCE are founded, are pointed out. It is shown that for such PT1 the fact of irreversibility must be taken into account in the theoretical calculations.

We propose to evaluate the value of irreversibility of PT1 by means of expression

$$NQ = ((\Delta V_m / \Delta S_m) \tilde{n} (dT_m / dP)) / (\Delta V_m / \Delta S_m) \quad (2)$$

It is obviously, this value is qualified the precision of consistent use of a thermodynamic formulas (which were obtained by means of the postulate of reversibility) to the real PT1. The value NQ also is qualified the accuracy of calculation by CCE one from three parameters PT1 (dT_m/dP , ΔV_m , ΔS_m), if the other two are measured. It is found that at the melting of AHC the deviations from CCE can reach a significant value: up to $NQ \approx 50\%$.

It turns out that just for such matters (where there occurs a sufficiently large value of NQ) the largest manifestations of the recently experimental discovered effect of "phase transitional radiation" (PR) are observed. The essence of the PR-effect consists in that under condensation or under crystallization of some materials (for water, some metals, and especially marked for AHC) one observes the sharp flash of infrared radiation. It is proposed to use the experimentally detected deviations from CCE for thermodynamic indications of the presence PR under PT1 in different materials.

It is indicated by means of CCE the Ehrenfest equation (EE), which describes the phase transitions of the second kind (PT2), can be obtained from the inequality (1) too. In this case it is necessary to take into account that at PT2 we have: $\Delta V_m \rightarrow 0$, and $\Delta S_m \rightarrow 0$, i.e. PT2 is the reversible process. But for PT2 is the irreversible process, then at the heating and at the cooling along an isobar we shall receive different critical point parameters. However it isn't observed under experiments. It is proven that PT2 is reversible, and EE for PT2 is the identity equality.